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54) Title: MANUFACTURING (PREPARATION) OF pH-SENSITIVE MICRO-CAPSULES

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Detailed Description

1. Title **Manufacture of pH-sensitive microcapsules**

2. Patent Claims

1. Preparation of pH-sensitive microcapsules by employing a mixture of the following monomers:

(A) One or more kinds of basic monomers shown in formula (I)

(I)

(Where R is H or CH, and R^1 and R^2 are alkyls with C1 - C3, respectively.)

(B) One or more kinds of water-insoluble or sparingly soluble monomers.

(C) One or more kinds of water-soluble monomers.

The core substances are dispersed in a solvent containing the copolymer of (A) (B), and (C) in the dissolved form.. The resulting dispersion is mixed with oil and additional solvent and then the solvent is removed to produce microcapsules.

3. Detailed explanation of the invention

Application in industry

This invention is dealing with the preparation of microcapsules which are insoluble in alkaline solution but are soluble in neutral solution, i.e., microcapsules with pH-sensitive solubility. Thus, for example, they will be used as washing auxiliaries to alkaline detergents.

Background

It is possible to introduce desired materials at a certain

pH if the microcapsules are prepared by coating core substances with pH-sensitive materials.

For example, the microcapsules will be useful for washing auxiliaries when they are combined with an alkaline detergent. Generally, laundry washing machines are operated using the following processes: addition of water, washing, spin drying, rinsing, and then spin drying again. Thus, washing auxiliaries, such as fabric softeners, are added after washing. Hitherto, people operated washers step by step and it was not a burden to add washing auxiliaries such as softener, bleach, and/or starch before rinsing. The appearance of semiautomatic and fully automatic washing machines freed peopIe from those operations, however, it is still necessary to add the auxiliaries before rinsing.

What can we solve by this invention?

Washing auxiliaries in the form of capsules coated with polymer, which is insoluble in the alkaline washing solution but soluble in the neutral rinsing solution, will work only during rinsing even when they are introduced together with the detergent, since the capsules are insoluble in the washing solution due to its basicity.

It has been known that some polymers have pH-sensitive solubility. For instance, polyvinyl acetal diethylaminoacetate is insoluble in neutral water but soluble in water at a pH above 5.8. Furthermore, copolymers of vinylpyridine and acrylic acid are soluble in water of both at pH above 7.4 and below 4 while they are not soluble between pH 4 and 7.4. However, so far,

polymers having solubility only in neutral and acidic solution with ability to change their solubility in a narrow pH range, have not yet been prepared. Recently, the inventors have reported such copolymers and washing auxiliaries coated by those polymers in JP 83-247997.

When core substances such as washing auxiliaries are coated by polymers, they have to be coated completely to get the best result.

Sometimes, small particles must be coated. For instance, washing auxiliaries should remain on the textile after the washing and drying processes followed by rinsing. Thus they are required to be highly adsorptive on textiles and to have as small a size as possible.

Constitution of the invention

This invention has as its purpose to prepare microcapsules which are able to coat and protect the core substances in alkaline aqueous solution while discharge the core substances in neutral and acidic aqueous solution.

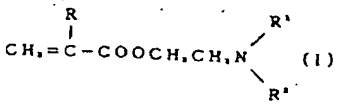
Furthermore, this invention will provide the directions for the preparation of microcapsules as small particles.

Namely, the invention is concerned with the preparation of pH-sensitive microcapsules via the following processes (a) and (b).

(a) The process of dispersion of core substances in a solvent containing copolymers of the following three monomers, (A),(B), and (C).

(A) one or more kinds of basic monomers shown in general

formula (I).



(I)

(where R is H or Me, and R^1 and R^2 are alkyl groups with Cl - C3, respectively.)

(B) One or more kinds of water-insoluble and/or sparingly soluble monomers.

(C) one or more kinds of water-soluble monomers.

(b) The processes of mixing the resulting dispersion from process (a) with oil and additional solvent and removal of the solvent serving as dispersion medium.

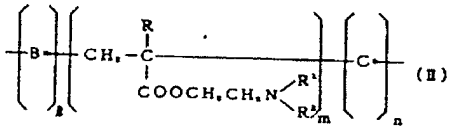
The basic monomers (A) shown in formula (I) are the crucial materials for the preparation of pH-sensitive copolymers. The following are examples of basic monomers and they will be used singly or in combinations; N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl acrylate, and N,N-diethylaminoethyl methacrylate.

The water-insoluble or sparingly soluble monomers listed in (B) are used to widen the pH range where the pH-sensitive copolymers are insoluble. One or more kinds of the following will be employed as monomers: acrylate, methacrylate, crotonate, itaconate, vinyl acetate and/or styrene. When alkyl esters of acrylic acid, methacrylic acid, crotonic acid, and/or itaconic acid are employed as monomers (B), the number of C atoms in the alkyl groups is recommended to be between 1 and 8, otherwise the dissolution rates are slow under slightly alkaline conditions. For example, methyl acrylate, ethyl acrylate, butyl acrylate, and

methyl methacrylate are preferred.

The water soluble monomers (C) contribute to increasing the soluble pH range and some representative compounds are as follows; N,N-dimethylaminopropyl acrylic (or methacrylic) acid amide, N,N-dimethylamino acrylic (or methacrylic) acid amide, 2-hydroxyethyl acrylic (or methacrylic) acid, 2-hydroxypropyl acrylic (or methacrylic) acid, and esters of acrylic (or methacrylic) acid and polyethylene (or methoxy polyethylene) glycol bearing 2 - 30 moles of ethylene glycol adducts (i.e. p = 2 - 30). One or more of the monomers (C) will be used.

The ratio of the monomers in the copolymerization can be varied to change the desired pH range where the microcapsules should be either soluble or insoluble. The microcapsules for washing auxiliaries are preferred to be insoluble in water at a pH above approx. 9.5 and soluble at a pH below approx. 8.5 even in the presence of detergents. Thus, $l/(l + m + n)$ = 0.08 - 0.45 and $m/(l + m + n)$ = 0.1 - 0.65 in formula (II) are suitable, and $l/(l + m + n)$ = 0. 1 - 0.4 and $m/(l + m + n)$ = 0. 15 - 0.55 are preferred.



(where B· and C· represent the units of monomer (B) and (C), respectively.)

The degree of polymerization (l + m + n) will be between 100 and 50,000, preferably between 300 and 20,000.

The copolymers used in this invention are prepared by

radical polymerization reaction under atmospheric or higher pressure. The following solvents can be used either by themselves, as a mixture, or with water: acetone, benzene, toluene, chloroform, ethyl acetate, isopropylalcohol, N,N-dimethylformamide, and dimethylsulfoxide. Two to 100 mmole equivalents of a radical initiator such as azobis(isobutyronitrile) and triphenylethylazobenzene with respect to the monomers are used.

The reaction conditions for polymerization depend on the solvent and/or on the combination of monomers, however, the reactions are generally carried out at 40 - 90°C for 5 - 20 hrs. The initial concentrations of the monomers also varies depending on the solvent, temperature and/or initiator. Usually, it will be 20 to 80 wt/wt %.

The microcapsules in this invention are produced by removing the liquid from a dispersion containing the core substances and pH-sensitive copolymers. First of all, the copolymers described above are dissolved in the solvent, followed by dispersing the core substances with stirring. As dispersion solvent, in which the copolymers are soluble and the core substances disperse, those mentioned for polymerization earlier and/or alcohols will be used. Especially, acetone is the best solvent. The concentration of copolymers in the dispersion solution is adjusted to 1 - 70 wt % and preferably 5 - 50 wt %. The amount of the core substances can be 0.2 - 10 times that of of the core materials.

Certain core materials would be chosen based on the purpose. The core substances for washing auxiliaries are as follows, with a diameter of 10 - 500 μm; fabric softener: di-long-

chain alkyldimethylammonium salts, 1-methyl-1-long-chain alkanoyl aminoethyl-2-long-chain alkylimidazolinium salt, a mixture of di-long chain alkyldimethylammonium salts and fatty acid salts. Antifoaming agents: silicone oil, etc. Bleach: hypochlorite, percarbonate, organic peroxide, etc. Starch, bluing agents, fluorescent brighteners and enzymes.

Then the resulting dispersion of the core substances is mixed with oil and additional solvent. As the oil, liquid paraffin, vegetable oil, etc., are used since these oils are liquid at room temperature. Liquid paraffin is especially recommended. There are many grades of liquid paraffin available for this purpose and those having a viscosity below 100 cst at 37.8°C are preferred.

The ratio of dispersion solvent/oil (wt/wt) is between 0.01 to 0.2 and 0.03 to 0.1 is preferred. A ratio under 0.01 will produce lumps and it takes a long time to remove the solvent with a ratio of over 0.2. The mixed solvent of oil and dispersion solvent does not have to be homogeneous. The ratio of dispersion solvent/mixed solvent is between 0.1 and 0.7 (wt/wt).

The microcapsules are obtained by evaporation of the dispersion solvent under either reduced pressure (20 - 60 cm Hg) at room temperature or 40 - 50°C or just by heating (40 - 60°C). The microcapsules are then collected by filtration, followed by washing.

Results

This is an invention to prepare microcapsules by using method of drying of the dispersion in a liquid.

The core substances are dispersed in a solvent containing copolymers, followed by the addition of mixed solvent of oil and another solvent. Upon evaporation of the solvent, the core substances become coated by the copolymers. The addition of oil instead of the mixed solvent will result in the formation of lumps, which is not useful for microcapsules. On the other hand, use of the mixed solvent gives the desired microcapsules which show pH sensitivity.

Effect

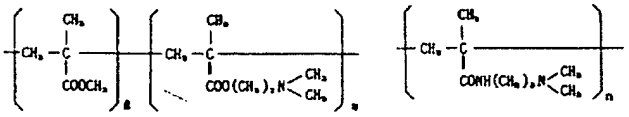
We have shown here an efficient preparation of microcapsules, which are insoluble in alkaline water while they are soluble in neutral and acidic aqueous solutions to discharge the core substances into water.

Thus, the microcapsules with washing auxiliaries as the core substances are very useful auxiliaries for alkaline detergents for textiles.

Examples

Example 1

Twenty g of distearyldimethylammonium chloride (powder, < 100 mesh) were suspended in 70 g of acetone solution containing 20 wt % of the water-soluble polymer shown below.



[l/(l + m + n) = 0.35, m/(l + m + n) = 0.45

l + m + n = 1800 - 1500]

The resulting solution was dispersed in a mixed solvent of

liquid paraffin (viscosity: 14 cst, 37.8°C, 600 g) and acetone (24 g) in 1 L four-neck flask with stirrer.

The mixture was stirred for 4 hr at room temperature under a pressure of 30 - 50 cm Hg. No lumps were observed during evaporation under low pressure. The particles were then filtered on filter paper, followed by washing with n-hexane to produce microcapsules of distearyldimethylammonium chloride with 20 - 200 µm diameter, coated by a water-soluble polymer. The microcapsules obtained are used as fabric softener washing auxiliaries.

Example 2

Instead of evaporation of the acetone under reduced pressure shown in the Example 1, the acetone was evaporated by heating at 50 - 55°C for 5 hrs with stirring. Microcapsules similar to those obtained in Example 1 were formed.

Comparison Example 1

The preparation of the capsules proceeded by the method of Example 1 in liquid paraffin instead of the mixed solvent of liquid paraffin and acetone. In this case, large lumps (a few cm in diameter) were formed instead of microcapsules.

Example 3

The preparation was carried out according to Example 1 with silicone oil instead of distearyldimethylammonium chloride and microcapsules having diameters of 50 - 300 µm were obtained without the formation of lumps. These microcapsules worked efficiently during the rinsing cycle.

Example 4

Microcapsules with diameters of 50 - 200 µm were made

according to Example 2 with sodium percarbanate (< 100 mesh) as the core substance instead of distearyldimethylammonium chloride. No lumps were observed.

PATENT ASSIGNEE	(LIOY) LION CORP
TITLE	Mfr. of ph-sensitive microcapsules - for delivering washing auxiliaries when wash water has desired pH
ACCESSION NUMBER	86-079084/12
ABSTRACT	The microcapsules are produced from (A) one or more kinds of basic monomer of formula CH2=CR-COOCH2CH2NR1R2 (where R is H or CH3 and R1 and R2 are each 1-3C alkyl). (B) one or more kinds of insoluble or slightly-soluble monomer and (C) one or more kinds of water soluble monomer are dissolved. Core substances are dispensed in a solvent contg. the (A), (B) and (C); the dispersion is mixed with oil and a further solvent and this further solvent is then removed to yield the micro capsules. Pref. (A) N,N-di-methyl-amino-ethyl acrylate, N,N-di-methyl-amino- ethyl metacrylate, N,N-di-ethyl-amino-ethyl acrylate, N,N-di-ethyl-amino-ethyl metacrylate etc. Pref. (B) is (m)ethyl (meth)acrylate. Pref. (C) is N,N-di-methyl-amino-propyl (meth)acrylic acid amide, 2-hydroxy-ethyl (meth)acrylic acid, polyethylene glycol (meth)acrylate etc. The microcapsules are adjusted to be insoluble in pH above 9.5 and to be soluble in pH up to 8.5. USE/ADVANTAGE - The microcapsules are insoluble in alkaline soln., but dissolve in neutral and acidic soln., releasing the core substances. The microcapsules are useful for washing textile and contains softening agents, bleaching agents, enzymes etc. (5pp Dwg.No.0/0)
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